

**Investigation of Spatial Heterogeneity in Ni Distribution Among Annual Rings of *Salix nigra* (black willow) Inhabiting a Former Radiological Settling Pond.**

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Beamline(s): X26A

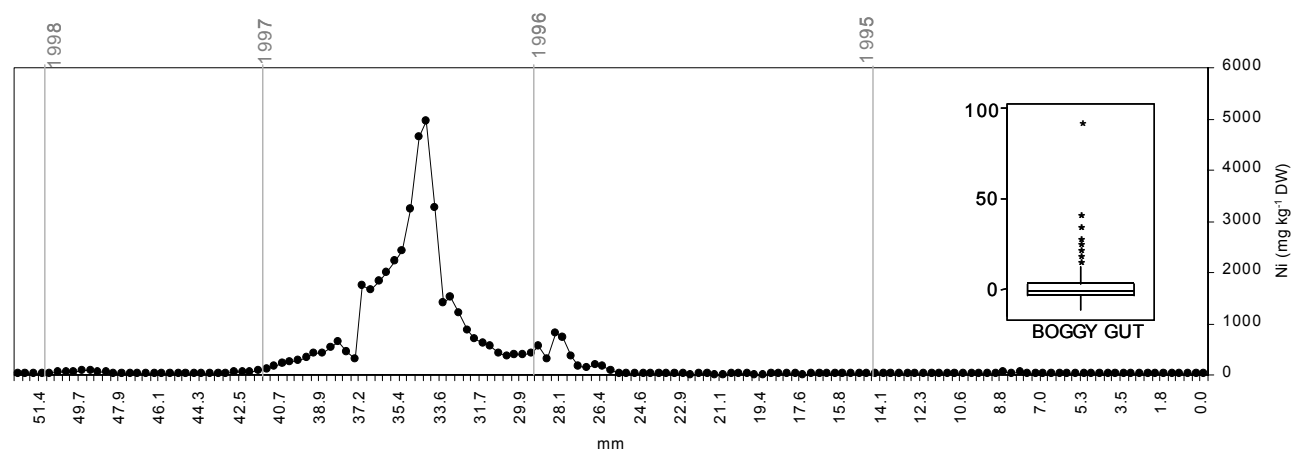
**Introduction:** Steed Pond (SP) is located in the northwest corner of the Savannah River Site (SRS), near Aiken, South Carolina. SP is an important former waste unit, not only for the amount of natural and depleted uranium ( $^{238}\text{U}$ ), nickel (Ni) and aluminum (Al) it contains, but also for the well documented history of breaches, which have allowed erosion of contaminants into the riparian environments downstream. Previous studies on willows (*Salix nigra* L.) collected downstream from SP have shown the presence and heterogeneous distribution of Ni within annual rings in years which strongly correspond with historical reports of breaches in waste unit integrity (PUNS258, NSLS 2001), suggesting that synchrotron X-ray fluorescence (SXRF) microspectroscopy is a valid technique for use in retrospective biomonitoring. This study aimed to show the differences in elemental abundances between the annual rings of trees growing on SP with those measured from impacted trees downstream, and investigates within-ring heterogeneity to further our understanding of how trees growing in contaminated environments transport and store metals within the xylem.

**Methods and Materials:** Tree cores were collected from mature *Salix nigra* L. (black willow) growing close to the breached spillway at SP, and a reference uncontaminated area upstream at a height of 14 and 36 inches from the base of the tree. Cores were collected with a Teflon-coated increment corer (20cm x 0.5 cm), dried (60 °C, 48h), and cut into 2 cm sections, maintaining orientation and then sliced longitudinally with a dissection blade to >1mm thick. Sections were mounted on metal-free KAPTON tape and analyzed by synchrotron-based X ray fluorescence (XRF) microscopy. 1D scans were carried out using tantalum shutters to collimate the beam to 300 × 300 μm, used a step size of 350 μm and a 90 second dwell time. 2D maps were generated from metal-rich regions using the same beam size; a 35 second dwell time per pixel and a smaller step size (250 μm). More detailed investigation of regions of interest (approximately 0.5mm<sup>2</sup>) were carried out using a beam size collimated to 10 × 10 μm with a rhodium coated Kirkpatrick-Baez focusing device, a dwell time of 6 seconds and a step size of 16 μm. Ion-chamber normalized XRF counts were converted to mg kg<sup>-1</sup> by calibrating with SRM 1575 (Pine needles). Replicate tree cores were aged via standard image analysis techniques. Historical environmental data (e.g. temperature, rainfall) was also referenced for the area.

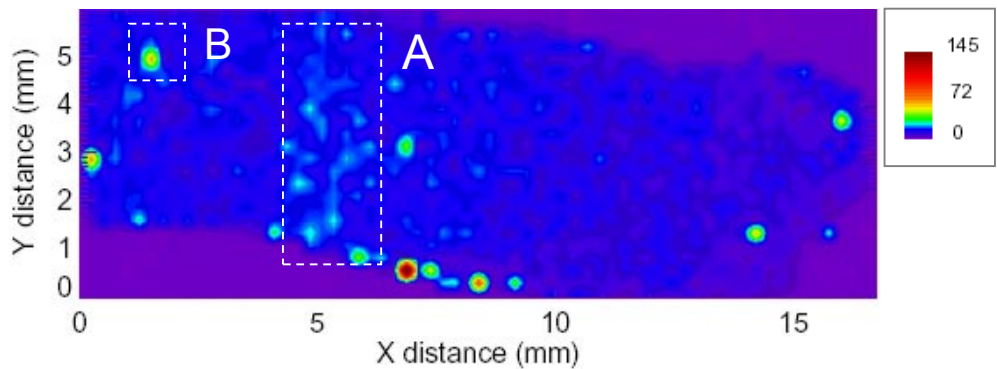
**Results:** *S. nigra* from SP contained far greater concentrations of Ni within annual rings than were observed in trees collected from the impacted depositional site downstream. In this case, concentrations of Ni reached approximately 5000 mg kg<sup>-1</sup> DW in highly localized areas of cores sampled from 36 inches from the tree base (Figure 1), in comparison with a maximum of ≈ 900 mg kg<sup>-1</sup> in trees downstream. Furthermore, cores collected from 14" from the base of the tree appeared to contain much higher Ni concentrations within the annual rings, although this requires further validation. Compositional maps of enriched regions show two different phases of enrichment; first a diffuse area that is consistent across the annual ring (Figure 2 (A)) and secondly, discrete points, which appeared to contain much higher concentrations of Ni (Figure 2(B)). These discrete points, measuring approximately 100 μm across, were chosen for closer investigation, and appeared to consist of high concentrations (900-1500 mg kg<sup>-1</sup>) of Ni (Figure 3). Extremely low concentrations of co-associated metals Cu and Zn in this region suggested it may be a purely Ni-containing anomaly. The tree at SP was approximately eight years old, and the Ni peak corresponded with 1996-1997; a year when rainfall was particularly low.

**Conclusions:** Willow trees inhabiting the former waste unit contain much higher concentrations of Ni within localized annual rings than trees growing within the influence of eroded SP sediments, further downstream. Results suggest that the concentration of Ni is higher in the woody tissue closer to the base, although further work is needed to confirm higher elemental abundances. Further, increases in Ni in the annual rings at SP appear closely bound to water availability at the site. Ni within annual rings appears in a diffuse form; possibly bound to negatively charged carboxyl groups within the xylem vessels, and a highly concentrated, discrete form. Further investigation showed that these discrete points of Ni are not structural elements but an exclusively Ni-containing anomaly present within vessel elements.

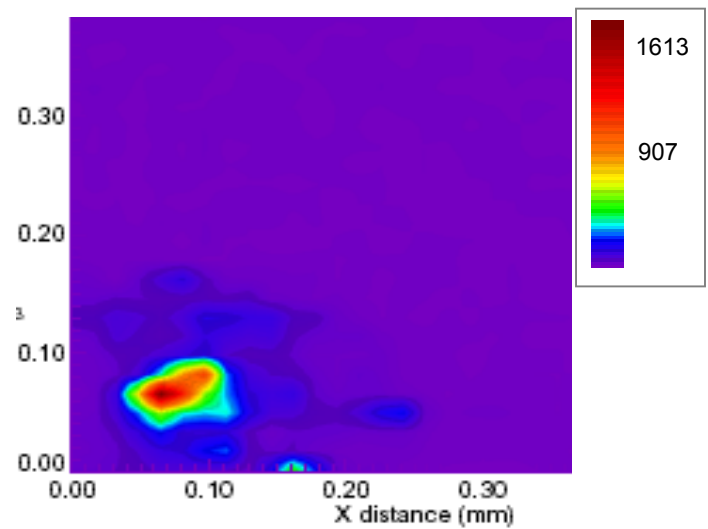
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**Figure 1.** Concentration of Ni located within the annual rings of *Salix nigra* L. from a former radiological settling pond, contaminated with U and Ni. Numbers in gray represent the year in which the annual ring was formed, as resolved by image analysis. Inset shows control data collected from the uncontaminated site upstream. Boxes represent upper and lower quartiles bisected by the median; whiskers represent the minimum and maximum observed concentrations and asterisks are outliers.



**Figure 2.** Two-dimensional compositional map of the enriched section of the SP tree core, showing A: the diffuse region of enriched Ni, and B: discrete areas of Ni enrichment. Legend shows mg kg<sup>-1</sup> dry wt. Ni.



**Figure 3.** Two-dimensional compositional map of the discrete Ni-enriched anomaly from Figure 2B, showing elevated, localized concentrations of Ni. Legend shows mg kg<sup>-1</sup> dry wt. Ni.